Preparation, characterization and electrochemistry of carbon nanotubes directly attached to Si(100) surfaces

Jingxian Yu*, Joe Shapter*, Jamie Quinton*, Martin Johnston*, and David Beattie†
*School of Chemistry, Physics and Earth Sciences, Flinders University, Bedford Park, SA 5042, Australia
Email: joe.shapter@flinders.edu.au
†Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia
Email: david.beattie@unisa.edu.au

***Abstract*—We present a new approach for directly organizing single-walled carbon nanotubes (SWCNTs) onto silicon surface. The ordered assembly of SWCNTs was made by the surface condensation reaction with hydroxyl terminated silicon. X-ray photoelectron spectra, Raman spectroscopy and atomic force microscopy show that the shortened SWCNTs have been organized successfully on silicon. The electrochemistry of SWCNT array exhibits good electrochemical reversibility and enhanced conductivity.**

Keywords-carbon nanotubes; silicon; electrochemistry; Raman spectroscopy; Atomic Force microscopy

I. INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) are elongated members of the fullerene family [1]. These one-dimensional molecular structures recently have become the focus of intense multidisciplinary study due to their unique structure, chirality-dependent conductivity, high mechanical strength and good chemical stability. These properties make carbon nanotubes excellent candidates for electron field emission sources [2], scanning probe tips [3], nanoelectronic devices [4], energy storage [5], actuators [6], chemical and biochemical sensors [7-9]. However, most of these potential applications require surface mounted aligned carbon nanotube arrays grown with large-scale control of location and orientation [10, 11].

Liu [11] and our group [12] have demonstrated the formation of short SWCNT assemblies oriented normal to a gold substrate through surface reaction. In view of the importance of silicon as the primary semiconductor material in modern microelectronic devices, efforts to control its electronic properties and to tailor the chemical and physical characteristics of its surface are of major importance. This paper will present the preparation and characterization of carbon nanotubes directly attached to silicon and the electrochemistry of the new structure. An understanding of the electrochemical properties of SWCNTs directly attached to silicon is essential with respect to their potential application in developing silicon-based electrochemical or bio-electrochemical sensors and ultra-microelectrodes arrays.

II. EXPERMIMENTAL

Highly boron doped p-type silicon (100) wafers (0.5 mm thickness, 1 mΩ.cm resistance and polished on one side) were purchased from Virginia Semiconductor, Inc. USA. The surfaces ($0.5\times0.5cm^2$ size) were ultrasonically cleaned in acetone (99.5%, Merck) for 30 seconds and flushed by copious Milli Q water (18 MΩ.cm). Subsequently the silicon pieces were immersed into 1:1:5 mixture of 30% NH_4OH (Sigma-Aldrich), 30% H_2O_2 (Sigma-Aldrich) and Milli Q water (18 MΩ.cm) for 15 minutes at 80°C, then into 1:1:5 mixture of 36% HCl (Ajax Finechem), 30% H_2O_2 (Sigma-Aldrich) and Milli Q water (18 MΩ.cm) for 15 minutes at 80°C [13]. The hydroxyl terminated silicon (Si-OH) was incubated in the 0.1mg/mL DCC and 0.12mg/mL shortened nanotubes (8 hours cutting in mixed acid, RFP-SWCNT, Carbon Solutions, Inc. USA)/DMSO (≥99.9%, Spectrophotometric Grade, Sigma-Aldrich) solution for different reaction times to make carbon nanotubes directly attached to silicon surfaces. Figure 1 shows the schematic representation of the preparation of SWCNTs directly attached to silicon.

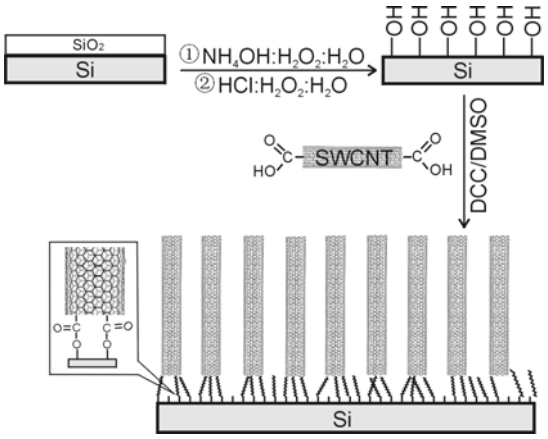

Figure 1. Schematic representation of the preparation of SWCNTs directly attached to silicon.

X-ray photoelectron spectra were obtained on an Axis Ultra (Kratos Analytical, UK) XPS spectrometer equipped with an Al Kα source (1486.6eV). A commercial Raman microscope (Renishaw Ramascope System 1000) was used to collect Raman scattered light. Atomic Force Microscope tapping mode

images were taken in air with a multi-mode head and Nanoscope IV controller (Digital Instruments, Veeco, Santa Barbara). Commercially available silicon cantilevers (FESP-ESP series, Veeco probes, Santa Barbara) with fundamental resonance frequency between 70-85 KHz were used. All electrochemical experiments were performed inside a dry-box filled with high purity N_2 using a BAS 100B Electrochemical Analyzer at room temperature.

III. Results and Discussion

A. X-ray Photoelectron Spectra

Figure 2 shows the X-ray photoelectron survey spectrum for the hydroxyl terminated silicon and the SWCNTs directly attached to silicon. Compared to the hydroxyl terminated silicon, the SWCNTs directly attached to silicon shows a strong C1s peak at 284 eV. The high resolution C1s spectrum of the SWCNTs directly attached to silicon is deconvoluted by Casa XPS software into 5 peaks at binding energy 284.6 eV, 286.1 eV, 287.4 eV, 289.1 eV and 290.7 eV. These bonds are assigned in turn to sp^2 C=C/sp^3 C-C, C-O, C=O, -COO[14] and π bond shake-up satellite peak for C1s in shortened nanotubes[15]. This is due to the fact that functionalised nanotubes have been oxidised in an oxidative mixed acid before the surface reaction and still have oxide functional groups at their free ends after attachment to the silicon surface.

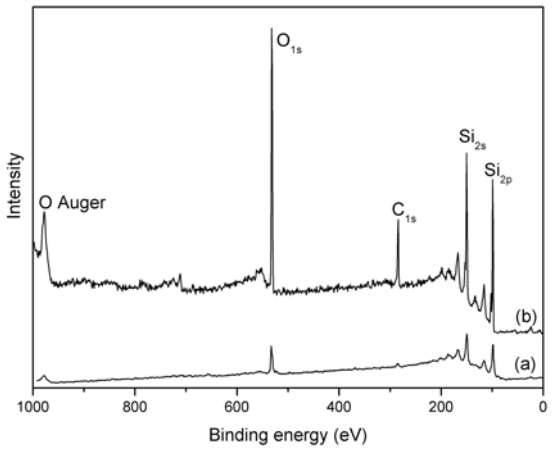

Figure 2. XPS spectra for the hydroxyl terminated silicon (a) and the SWCNTs directly attached to silicon after 20 hrs exposure at 80 °C (b).

B. Raman Spectroscopy

Figure 3 shows typical Raman spectra for the hydroxyl terminated silicon and SWCNTs directly attached to silicon, where the SWCNTs directly attached to silicon was prepared with 20 hours exposure at 80 °C. For the hydroxyl terminated silicon, we can only observe a broad band at 950 cm^{-1}, which is due to bulk silicon. By comparison to the hydroxyl terminated silicon, the SWCNTs directly attached to silicon spectrum has two resonance-enhanced Raman bands at 1595 cm^{-1} and 1314 cm^{-1}. The difference spectrum is shown as curve (c) in Figure 3. Two peaks appearing on curve (c) are well-known as the tangential band (G band) and the disorder-induced band (D band) for single-walled carbon nanotubes [16, 17]. The G band provides information about the chirality of SWCNTs, where different chiralities yield either semiconducting and metallic nanotubes. The D band on the other hand provides information on the purity of the carbon nanotubes and how ordered the graphene structure of the nanotubes are, as the size of the peak gives an indication of the amount of amorphous and poorly organized material is present in the sample [16, 18]. In Figure 3c, the ratio of D/G is 0.31, which is considerably larger than the values of 0.01 for the isolated as-prepared single-walled carbon normally [16], and 0.1 for the vertically aligned SWNCT arrays prepared by molecular beam-controlled nucleation and growth [19]. We envisage that the larger D/G value can be attributed to the defects on the sidewall of carbon nanotube caused by cutting process in mixed acids.

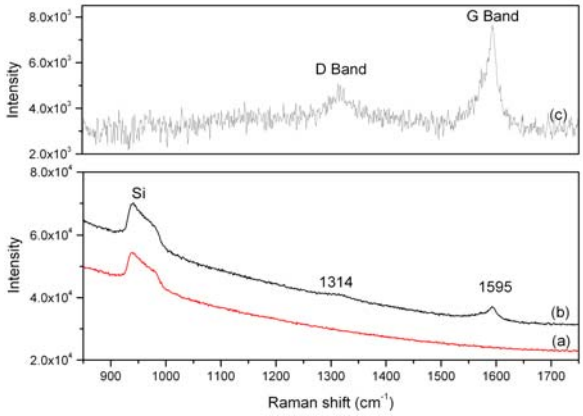

Figure 3. Typical Raman spectra using a λ=785nm laser line for hydroxyl terminated silicon (a) and SWCNTs directly attached to silicon (b). Curve (c) is the difference spectrum obtained by subtracting Curve (a) from Curve (b).

C. Atomic Force Microscopy

Figure 4 shows tapping mode AFM images for SWCNTs directly attached to silicon surface with different exposure times. Before attachment of functionalized carbon nanotubes, the hydroxyl terminated silicon pieces are flat surfaces. After the surface condensation reaction, however protrusions are clearly observed in AFM images (Figures 4a-c). At the short exposure time (2 hours, shown in Figure 4a), well separated carbon nanotube islands can be seen with large areas of bare silicon surface. However with longer exposure time, more and bigger carbon nanotube islands appear on the silicon surface, and the bare silicon area decreases. The coverage for different exposure time has been measured to be 36%@2h, 85%@20h and 90%@100h. The average island diameters are 95nm@2h, 110nm@20h and 140nm@100h. The larger diameter is due to the fact that carbon nanotubes tend to bundle together and form clusters at the applied assembly temperature. The average heights are 22.85nm@2h, 29.8nm@20h and 35.49nm@100h. The maximum heights observed in each AFM image are 41.06nm@2h, 71.99nm@20h and 101.49nm@100h again increasing with reaction time as expected.

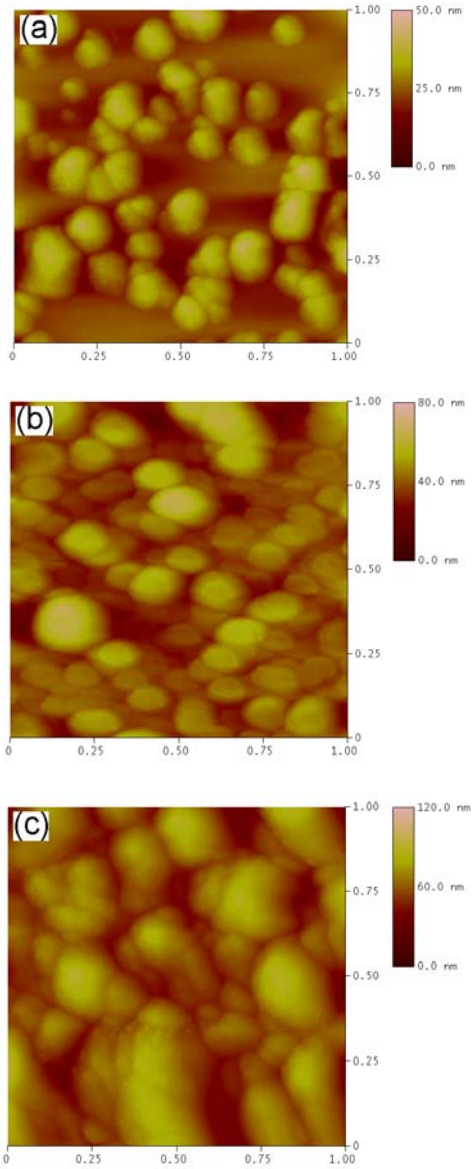

Figure 4. Tapping mode AFM images for the SWCNTs directly attached to silicon surfaces under different exposure time at 80°C, where (a) 2 hours, (b) 20 hours and (c) 100 hours.

D. Electrochemistry

Figure 5 shows the cyclic voltammograms (CVs) for SWCNTs directly attached to silicon and hydroxyl terminated silicon in 0.1 mmol L^{-1} ferrocene dissolved in 0.1 mol L^{-1} TBAP/CH_3CN solution as well as a CV for SWCNTs directly attached to silicon in a TBAP/CH_3CN blank solution. For the SWCNTs directly attached to silicon in ferrocene/TBAP/CH_3CN solution shown in Figure 5a. Clearly evident are distinct redox waves with anodic and cathodic peak positions at 474 mV and 596 mV respectively. The oxidation of ferrocene to the stable ferricenium cation is a simple one-electron transfer reaction, in that there are no complications arising from adsorption or associated chemical reactions. Compared to the cyclic voltammogram for a gold electrode in the same ferrocene/TBAP/CH_3CN solution (inset shown in Figure 5), the oxidation/reduction peak potentials on SWCNTs directly attached to silicon are comparable to those on gold electrode. When the SWCNTs directly attached to silicon was immersed in the blank solution without ferrocene, the CV looks very flat, indicating that only capacitive current can be observed. This result further proves that the redox waves shown in figure 5a are attributable to the oxidation/reduction of ferrocene in the solution. In addition, the cyclic voltammograms on hydroxyl terminated silicon were measured and are shown in figure 5c. In this case, a broad reduction peak at 150mV is observed but no obvious oxidation peak even under more positive switching potentials. Compared to the cyclic voltammograms on hydroxyl terminated silicon, SWCNTs directly attached to silicon yields electrochemistry with much better reversibility and enhanced conductivity compared to the bare substrate.

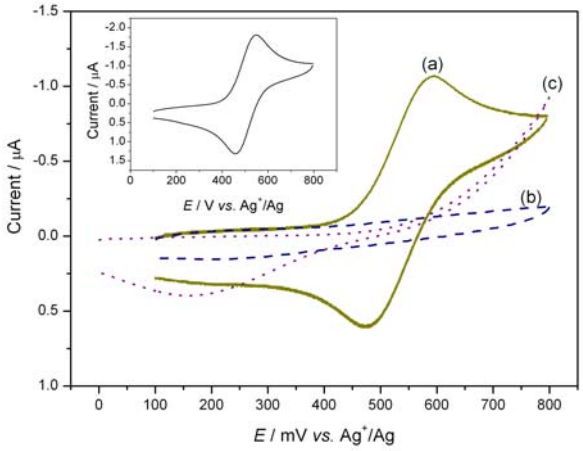

Figure 5. Cyclic voltammograms of SWCNTs directly attached to silicon (a) and hydroxyl terminated silicon (c) in 0.1 mmol L^{-1} ferrocene in 0.1 mol L^{-1} TBAP/CH_3CN solution, and SWCNTs directly attached to silicon in 0.1 mol L^{-1} TBAP/CH_3CN blank solution (b) at scan rate of 100mV s^{-1}. The inset shows the cyclic voltammograms on gold electrode in 0.1 mmol L^{-1} ferrocene in 0.1 mol L^{-1} TBAP/CH_3CN solution at scan rate 100mV s^{-1}.

Figure 6 shows the cyclic voltammograms of SWCNTs directly attached to silicon in 0.1 mmol L^{-1} ferrocene dissolved in 0.1 mol L^{-1} TBAP/CH_3CN solution at different scan rates. It is apparent that the oxidation/reduction current peaks get bigger with the increase in scan rate. The inset shown in Figure 6 shows the dependence of anodic peak current on the square root of scan rate. The straight line suggests that the oxidation/reduction process is controlled by semi-infinite linear diffusion of ferrocene to the interfacial reaction zone. At the same time, the peak-to-peak separation ΔE_p becomes larger with increasing scan rates, which is consistent with a quasi-reversible electrochemical reaction. ΔE_p was recorded at different scan rates (10-1000mV s^{-1}). The electron transfer rate constants k_s were calculated from the dependence of the ΔE_p on the dimensionless kinetic parameter Ψ, according to the theory developed by Nicholson [20]. Assuming the diffusion coefficient for ferrocene in acetonitrile, D_R, is equal to that of ferricenium cation, D_o, and the transfer coefficient is α=0.5, the rate constants were calculated at different scan rates assuming $D_R = 2.4\times10^{-5}$ cm^2 s^{-1} [21]. The average rate constant for SWCNTs directly attached to silicon in 0.1 mmol L^{-1} ferrocene dissolved in 0.1 mol L^{-1} TBAP/CH_3CN solution is 4.54×10^{-3} cm s^{-1}.

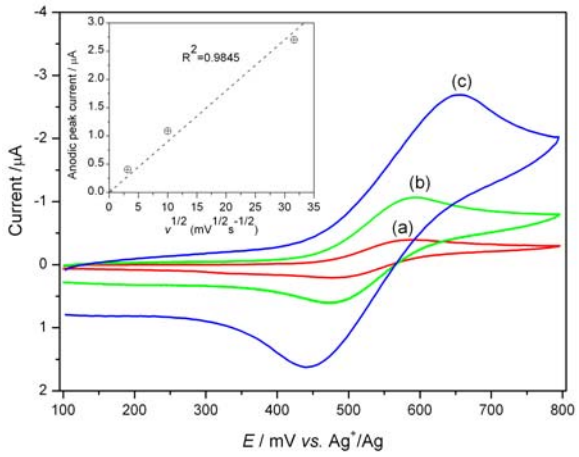

Figure 6. Cyclic voltammograms of SWCNTs directly attached to silicon in 0.1 mmol L^{-1} ferrocene dissolved in 0.1 mol L^{-1} TBAP/CH_3CN solution at different scan rates, (a) 10 mV s^{-1}, (b) 100 mV s^{-1} and (c) 1000 mV s^{-1}. The inset shows the dependence of anodic peak current on the square root of scan rate.

In order to compare rate constants under the same experimental conditions, the rate constant on gold was estimated using peak separations to be 1.32×10^{-2} cm s^{-1} at scan rate 100mV s^{-1} based on the inset shown in Figure 6. This value is 2-3 times larger than that on SWCNTs directly attached to silicon. The results indicate that SWCNTs directly attached to a silicon electrode possess a sufficient density of states to support relatively rapid electron transfer kinetics. This means that potential applications such as the fabrication and development of silicon-based electrochemical and bio-electrochemical sensors are certainly feasible.

IV. Conclusions

We have successfully demonstrated a new approach for the fabrication of vertically aligned shortened carbon nanotube architectures on a silicon (100) substrate by direct chemical anchoring. Compared to other techniques, this new technique has several advantages including the low temperature involved and the possibility for further modification. Electrochemistry using the new interface demonstrates excellent conductivity to the substrate meaning this approach has numerous potential applications. The attachment of the SWCNTs directly to the silicon surface provides a simple and new avenue for the fabrication and development of silicon-based electrochemical and bio-electrochemical sensors, solar cells and nanoelectronic devices using further surface modification.

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